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AMMONIUM PERCHLORATE LINEAR PYROLYSIS  
BY CONVECTIVE SURFACE HEATING

TECHNICAL REPORT ME-RT 69005

by  
Robert F. McAlevy, III and Richard B. Cole

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DEPARTMENT OF THE NAVY  
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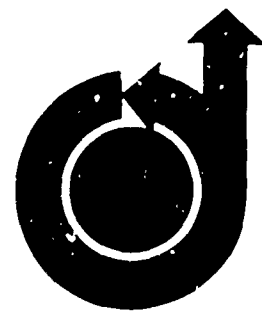
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AMMONIUM PERCHLORATE LINEAR PYROLYSIS  
BY CONVECTIVE SURFACE HEATING\*

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Abstract

Ammonium perchlorate (AP) specimens were exposed to various levels of convective surface heating at one atmosphere ambient pressure. Surface regression rates were measured and, simultaneously, surface temperatures were determined by measuring the infrared emission near  $3.1 \mu$ . These data represent the first AP linear pyrolysis characteristics obtained by means of convective surface heating. Previously, linear pyrolysis was obtained by pressing specimens against heated plates (solid and porous) and heated wire meshes. The subject data agree with some, and disagree with other, of these previous data.

The usefulness of convective surface heating and radiometric techniques are evaluated. It is demonstrated that preliminary experiments are required to support their use in linear pyrolysis studies. According to the evaluation, previous radiometric work dealing with surface decomposition is open to substantial question. It is concluded that the subject techniques are viable and offer experimental compliments to other methods, but that none of the current techniques are without substantial shortcomings.

Means of incorporation of AP linear pyrolysis results into theoretical models of the propellant deflagration process are discussed.

I. Background & Introduction

During the deflagration of composite solid propellants, the regressing propellant surface may be in the neighborhood of  $500^{\circ}$  to  $600^{\circ}$  C with a subsurface temperature gradient of  $10^3$  to  $10^5$  K/cm and a regression rate of 0.1 to 1.0 cm/sec (for pressures between 1 and 100 atm.). Under these conditions, gasification processes at the solid propellant surface are necessarily central boundary conditions in any realistic model of the deflagration mechanism.

Current models of propellant deflagration generally express the surface-gasification boundary condition as an algebraic relation between the surface regression rate of the propellant (or one of its ingredients),  $r$ , and the surface temperature,  $T_s$ . Such characterizations are presently included in models of both steady-state deflagration and of transient processes such as acoustic and non-acoustic instability, extinguishment, ignition, and flame spreading. Virtually without exception, the relation between  $r$  and  $T_s$  in such models has been of a quasi-steady, chemical kinetic form, that involving the familiar Arrhenius expression.

Attempts by others have aimed at providing both empirical correlations and theoretical bases for relating  $r$  and  $T_s$  under conditions approaching those of practical propellants. Chaiken, Andersen, and co-workers (1) and later, others (2-5) have made investigations of thermal decomposition (pyrolysis) at temperatures closer to the temperatures encountered during deflagration than are the temperatures of classical "bulk" pyrolysis (isothermal decomposition) studies.\*\* Via intense surface heating (resulting in temperature rise only near the surface of the material of interest), these investigations allow measurement of both the regression rate,  $r$ , of the heated surface and the "surface" temperature,  $T_s$ . Such regression of a near-planar, intensely heated, condensed-phase surface because of thermal decomposition has been termed "linear" pyrolysis.

Linear pyrolysis of propellant ingredients typically results in regression rates which are one or two orders of magnitude below those of propellants due to experimental limitations. Such pyrolysis rates and associated rates of temperature rise may, however, be orders of magnitude

\*The work reported was sponsored by the Office of Naval Research under Contract Nonr 263 (48).

\*\*In a bulk pyrolysis process, the decomposing specimen is essentially isothermal, and therefore, reactions may occur throughout the bulk of the specimen with diffusion of reaction products to the specimen surface.

higher than those of bulk pyrolysis. As has been stressed numerous times in the past, there is no obvious relation between the phenomena of "bulk" and linear pyrolysis (6) or between bulk pyrolysis and deflagration (7).

During the subject program, the linear pyrolysis of AP\*, the most common propellant oxidizer, was studied experimentally in an attempt to check, by an independent experimental technique, the results of others. The aim of the work was also to produce less-scattered linear pyrolysis data than those reported by others.

## II. Prior Studies Of The Linear Pyrolysis Of Ammonium Perchlorate

In summarizing a great deal of work concerning conditions at the AP surface during combustion, Powling at ERDE in England has presented a resume of most of the prior linear pyrolysis rates on AP (8). Lieberherr at O.N.E.R.A. in France has since reported additional, current studies (4,5). The work reported in all cases deals with linear pyrolysis driven by either:

- (1) heated metallic surfaces pressed into intimate contact with the pyrolyzing AP surface [solid and porous "hot plates" (1-4) or wire meshes (5)].

or:

- (2) diffusion flames established above the pyrolyzing AP surface via impinging or parallel fuel gas streams (8,9).

The first of these approaches suffers the major disadvantages of:

- (i) possible mechanical and/or fluid mechanical disruption of the pyrolyzing surface,
- (ii) possible chemical interaction with the pyrolyzing material,
- (iii) inherent masking of the pyrolyzing surface from photographic or visual access during pyrolysis, and,
- (iv) the necessity of measuring surface temperature with a thermocouple on or within the heated metallic surface.

The first disadvantage has been noted earlier (10,11), as have the second (12) and the fourth (10). The significance of the third is apparent when it is noted that surface cracking of AP specimens is not uncommon (13).

The second approach eliminates all of these cited disadvantages and might well bear development beyond its current state which apparently yields considerable data

scatter. The diffusion-flame technique may, however, be excessively limited in its range of operation by flammability limits (11).

The data derived from linear pyrolysis techniques other than the most recent of Lieberherr are summarized in Fig. 1 where only the envelopes of highly scattered data and single lines representing less scattered data are shown. Allowing that the temperature data of Guinet are probably somewhat high (as reported by Lieberherr; Ref. 5, p. 2), these data, in combination, appear to be consistent and in some measure of agreement (8) considering the rather wide scatter in some of the data. Lieberherr mentions (5) some apparently unpublished data which is also in general agreement with the data of the others (4).

The most recent results (at nominally atmospheric and subatmospheric pressures) reported by Lieberherr are shown in Fig. 2 where the extent of the data of Fig. 1 is also indicated. The implication by Lieberherr (5) that these newer data are in good agreement with the previous data from him and others does not appear warranted.

## III. Experimental Approach

As a possible compliment to the previously - described linear pyrolysis techniques and as an independent check on previous results, a new linear pyrolysis technique for AP has been developed. The technique, used earlier with polymeric pyrolysis specimens (7,14), involves convective heating of the AP specimen by a hot gas jet and monitoring of the infrared emission from the pyrolyzing surface as a measure of surface temperature. Figure 3 depicts the overall experimental arrangement and Figure 4 details the specimen holder.

The advantages which accrue to this pyrolysis method are the same as those already attributed to the diffusion flame approach (relative to the other techniques used previously). In addition, optical access to the pyrolyzing surface is improved (relative to the diffusion flame approach) by eliminating the need for a high-temperature diffusion flame as a driving force for heat transfer to the surface. Convective heating provides "scrubbing" of pyrolysis products away from the gas layer above the pyrolyzing surface which gives the convective heating technique added value relative to the diffusion flame technique. Reducing the quantity of high-temperature pyrolysis products above the pyrolyzing surface reduces the amount of gas-phase emission, a factor which can interfere with radiometric surface-temperature measurement (9). The main disadvantage of the infrared method is the need for knowing the spectral emittance of the radiating, pyrolyzing surface.

\* Ammonium perchlorate

### AP Specimens

The AP specimens used in the work reported here were made by pressing 16-micron AP powder (hammer-milled from commercial, uncoated stock)\* at a nominal pressure of 16,000 psi. The pressings (ca. 3" x .4" x .25") were exposed to a water-saturated, room-temperature air environment for 2 to 3 days and then dried for several days in a desiccator. Following this treatment, the pressings were formed into circular cylinders of .156" + .002" diameter, and .5" to 1." length. The moisture-treatment and drying have been found to minimize breakup of the sample during testing and to yield specimens which exhibit the same pyrolysis rate and surface temperatures as specimens pressed at higher pressures (50,000 to 100,000 psi) by others.\*\*

The sample diameter was selected so as to be small enough to allow its end to be uniformly heated by the 0.20" diameter hot-gas jet available from an existing laboratory gas rocket (14). To allow rational selection of specimen diameter, assessment of the area of uniform heating by such a jet was made by impinging the jet on large, flat Plexiglas specimen and measuring the area over which the Plexiglas ablated to a uniform depth during short firings of the gas rocket.

Specimen diameter was carefully controlled in order to provide a close-fit between the specimen and the bore of the specimen holder. Such a close fit (+.002") was found sufficient to preclude hot-gas jet penetration between the specimen and its holder. Such penetration had been found earlier in this program to be a cause of specimen breakup during firing.

### Apparatus

The gas rocket was fired with methane and O<sub>2</sub>-enriched (37% O<sub>2</sub>-N<sub>2</sub>) under conditions close to those used previously (oxidizer supply pressure: 112 psig; fuel supply pressure: 90 to 112 psig; Ref. 14). These conditions provide for lean mixtures in the combustion chamber. In this range of operating conditions, gas jet velocities of about 1300 ft/sec to 1700 ft/sec. were measured with an impact tube and temperatures of about 815°C to 1150°C (uncorrected for radiation loss) were measured using platinum/6% rhodium-platinum/30% rhodium thermocouple of about 0.010" bead diameter.

An unmodified Perkin-Elmer Model 112 spectrometer was used to monitor infrared emission from the surface. The spectrometer included a double-pass Littrow

monochromator with thermocouple detector, NaCl prism, amplifier, and chart recorder. Radiant fluxes were measured over a spectral slit width (half-energy) of 0.069 microns (physical slit width: 250 microns) centered at a wavelength of 3.1 microns, the center of a resonant absorption band of the ammonium ion. This center wavelength was selected to minimize optical transparency of the pyrolyzing surface and because an infrared "window" was found near this wavelength in the gas-rocket exhaust jet. The spectral slit width is approximately one-third the spectral width of the absorption band as indicated by thin film transmission data at low temperatures (ca. 100°C, (9)). The slit height used was about 0.06" which gave, with the 250 micron physical slit width, a 3/4 - reduced-size slit-image at the specimen because of the external optics used. The optical axis of the emitted radiation which was monitored was inclined at about 65° to the surface normal to allow the monitored radiation to clear the gas rocket (see Fig. 3).

During test runs, the AP specimens were advanced manually using a lead-screw and push-rod to maintain the pyrolyzing surface in the plane of the specimen-holder plate (Fig. 4). Position of the sample was recorded as a function of time using a potentiometric, linear-motion transducer and a chart recorder.

### Test Procedure

Before firing, an AP specimen was inserted in the sample holder with the flat end of the cylindrical specimen lying in the plane of the sample-holder plate. With fuel and oxidant supply pressures set at the desired levels, the sample-holder-gas rocket system (mounted on a single base-plate) was ready for immediate firing. Before moving this system into position relative to the spectrometer, a black-body source (Barnes Eng'g. Model 11-200) was positioned in view of the monochromator to provide reference levels with which the detector signals during firing could be compared. The source was successively set at temperatures giving radiant fluxes (spectrometer signal levels) which bracketed that expected during the pyrolysis test. The black-body was then removed, the test system was moved into view of the monochromator, the run was made (with simultaneous recording of radiant flux levels and specimen position vs. time), typically for 1-1/2 to 2 minutes, and the black-body source was replaced for a check of the originally-recorded reference levels. The last step was necessary as a check that the window near the test specimen had not

\*This material was provided by the Solid Propellant Laboratory, Princeton University.

\*\*These comparison samples were graciously provided by M. Barriere of O.N.E.R.A. and R. Friedman of A.R.C.

fogged during the test and that excessive drift of the instrumentation system had not occurred during firing.

#### Data Reduction

Typical records of reference radiation levels and test radiation levels as obtained from the chart recorder of the spectrometer are shown in Fig. 5. In Fig. 6, a typical displacement-time record for the specimen is shown.

Linear-pyrolysis regression rates were determined by measuring an average (visual) slope of the displacement-time records over the duration of the test.

Lower limits for the surface temperatures during pyrolysis ( $T_S$ ) were determined. This was done by assuming a surface emittance ( $\epsilon_\lambda$ ) of unity and by interpolating appropriately between the reference (black-body) radiation levels ( $I_{\lambda,B}$ ) to determine the black-body temperature ( $T_B$ ) which would yield the same emission as that of the pyrolyzing surface ( $I_\lambda$ ):

$$\frac{I_\lambda(\epsilon_\lambda, T_S)}{I_{\lambda,B}(T_B)} = 1 = \frac{\epsilon_\lambda B_\lambda(T_S)}{B_\lambda(T_B)} \leq \frac{B_\lambda(T_S)}{B_\lambda(T_B)}$$

where  $B_\lambda(T)$  is Planck's (spectral) specific-intensity function expressed on a wavelength basis (15). From this then:

$$T_S \geq T_B$$

The radiant flux level characteristic of the average regression rate for each run was taken to be an average (visual) of the fluctuating and varying levels shown on each record.

More reasonable limits for the surface temperatures implied by the infrared emission measurements were also made using the data on normal AP emittance measured by Powling (8,9). Current efforts in the authors' laboratory are aimed at checking and extending these data from Powling relative to such potentially important concerns as surface roughness, subsurface structure, etc. Until these measurements are completed, however, Powling's results offer the only rational basis for deducing "true" surface temperatures from the radiometric data from AP. As a reasonable upper limit on the surface emittance, Powling's

most recently reported emittance value was chosen (0.83) (Ref. 16). This value was measured normal to heated AP surfaces (200° to 360° C), and the emittance is reportedly nearly independent of temperature. As a reasonable lower limit for the emittance in the present circumstances, Fresnel's reflection law (17) for optically flat surfaces of optically absorbing materials was used. With Powling's estimate of the absorption coefficient of AP at 3.1 microns ( $K = 15,000 \text{ cm}^{-1}$ ; Refs. 8,9) and a conservative estimate for the index of refraction of AP at the same wavelength ( $n = 1.00$ ), the ratio of normal and oblique spectral emittances was established for the emission direction used in the present experiments (65° to the normal). This value (0.87) times Powling's normal emittance value (0.83) gave a lower bound for the emittance characteristic of the authors' measurements (0.72).

#### IV. Results

Figure 7 shows an "Arrhenius plot" of the results of the pyrolysis experiments reported here. Indicated are the regression rate - surface temperature trends implied by the values of surface emittance discussed above. Shown superimposed is an envelope of the earlier results of others. In comparison with Fig. 1, the data of this study are seen to lie somewhat above Powling's scattered results (11), farther above Guinet's original results (3), and in the midst of Anderson and Chaiken's (1), Coates' (2) and Lieberherr's (4) scattered data. Guinet's data are subject to overestimation of the surface temperature (cited by Lieberherr, Ref. 5) and Powling's to overestimation owing to possible emission from the diffusion flame above the surfaces being viewed\*\*. In this light, the current results are very reasonable, though they are subject to further refinement of the emittance data on which they are based. The present data are also less scattered than the earlier data.

#### V. Relation of Current Results To Prior Linear Pyrolysis Studies

As pointed out above, the current results were envisioned as a compliment and an independent check on previous results obtained using different pyrolysis methods. Powling, in viewing a comprehensive collection of linear pyrolysis data for AP, suggested that an apparent activation energy\*\*\* of about 20 Kcal/mole seemed to fit the data well (8). A similar suggestion has been

\*This approach is based on the premise that scattering of infrared radiation within the pressed AP samples is unimportant. Powling's data for the transmittance of an 80-micron-thick, pressed AP specimen (9) support this premise.

\*\*It must be noted that the present results are not exempted from influences of gas-phase emission. The magnitude of such an influence is very difficult to check experimentally, but, as pointed out below (p. 5), there is reason to believe that the convective heating-infrared radiometry method minimizes such an influence.

\*\*\*See footnote next page

voiced by workers at ARC (6) and by Hall and Pearson (18). These suggestions allowed, however, that the scatter of the data involved did not positively exclude a higher value for the activation energy. A 30 Kcal/mole value is of interest because of its apparent significance in both deflagrating AP-fuel systems (rather than pyrolyzing AP systems) and in the variety of reactions observed in bulk pyrolysis experiments (8).

The work reported here appears to corroborate the previously suggested value of 20 Kcal/mole for the apparent activation energy, as indicated in Figure 7. In contrast with earlier, scattered results, the present data are quite reproducible, though presently more limited in range. Thus, these results, while subject to extension in range (a current effort) give a much clearer indication of a 20 Kcal/mole activation energy than do even wider-range earlier results.

Previous suggestions of this 20 Kcal/mole value by Powling, the group at A.R.C., and by Hall and Pearson all were heavily weighted by the low-scatter results of Guinet. These results, as pointed out above, have since been invalidated by Lieberherr. However, the present results serve as a new basis for support of the 20 Kcal/mole value, especially so since they derive from an independent experimental method.

The only reported data on the linear pyrolysis of AP which seemingly indicate an activation energy substantially different from 20 Kcal/mole are the recent results of Lieberherr (5). As shown in Fig. 2, Lieberherr's results imply an activation energy of about 7 Kcal/mole for  $1/T_s \leq 1.1 \times 10^{-3}$  and of about 33 Kcal/mole for  $1/T_s \geq 1.32$  to  $1.46 \times 10^{-3}$ . In this light, the regime of surface temperatures studied in the present work and in other prior work would have to constitute a "transition regime" i.e., a region between what Lieberherr terms high-and-low-temperature pyrolysis. The absence of any obvious dependence of activation energy on temperature in the present and prior results (excepting Lieberherr's most recent) is difficult to rationalize if indeed the data fall in a transition regime. The

authors are forced to conclude that Lieberherr's view of this matter is not currently supportable.

In summary, the present data serve to strengthen considerably the previous indications of an apparent activation energy for the linear pyrolysis of AP close to 20 Kcal/mole in the surface temperature range from 450° to 550° C and over pyrolysis rates of about 0.01 to 0.03 cm/sec.

#### Sources of Error In The Present Results

The two major potential error sources in the pyrolysis method reported here both concern the radiometric method employed for surface temperature measurement: First, uncertainty in the emittance of the pyrolyzing surface, and second, the possibility of contributions to the measured radiant fluxes by emission from the gas immediately above the pyrolyzing surface.

While the first possibility for error is currently under investigation by the author, a comment on it is in order. Unless the emittance of pyrolyzing AP surfaces is a fairly strong function of surface temperature, the presently implied activation energy is not subject to error because of uncertainty in emittance values. Different, constant values of the emittance result in the same slope on plots such as Fig. 7. Only changes of emittance with temperature will effectively alter the slope and, hence, the implied apparent activation energy. There is some evidence, furthermore, that the emittance of AP specimens is not a strong function of temperature, at least at low temperatures (9).

The second potential source of error cited, that of gas-phase emission, is troublesome and difficult to check experimentally. Using data from the high-pressure deflagration of AP (21), Steinz, Stang, and Summerfield have estimated (22), as have others (21), that the gas-phase reaction between ammonia and perchloric acid (the presumed products of AP gasification) occurs very close to the gasifying AP surface, e.g., 10 microns at 1 atm. If such is the case, emission from the gas phase in the present experiments can be expected to be quite small since the mass of gas participating is quite small. The emission from the thin gas layer between a gasifying AP surface

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\*\*\* The activation energies implied by linear pyrolysis experiments are termed hereafter "apparent". As has been discussed in the literature (e.g. Ref. 19), reactions which occur in non-uniform composition fields may evidence overall reaction rates and hence apparent activation energies which are not determined by individual rates processes (e.g., phase transition, a single chemical reaction, mass and heat diffusion) but by a combination of such processes. Such may be the case for linear pyrolysis as Chaiken has attempted to show for one case (20).



and the plane of completion of the ammonia-perchloric acid reaction can be estimated at appreciably less than 2% of the total emission at 3.1 microns wavelength from the gas plus the solid surface\*\*. While such a calculation suggests that gas-phase emission may not result in appreciable errors in the present study, such a conclusion is, tentative, at best, pending further estimates of such emission. However, in light of the general agreement between the present and earlier results, it can be anticipated that this error will prove to be small.

The possibility of the thin reaction zone mentioned immediately above has linear-pyrolysis implications beyond that of the error introduced by infrared emission from the zone. If such a thin reaction zone occurs at atmospheric pressure, it can feed heat to the surface during linear pyrolysis experiments. The question then arises as to whether linear pyrolysis experiments characterize surface processes only or surface processes which are heat-transfer coupled with a thin reaction zone. This question is currently unresolved and is particularly relevant to comparisons between hot-plate and convective-heating pyrolysis experiments. Measured hot-plate temperatures might be expected to differ even more from actual surface temperatures than previously estimated (10) if a near-surface reaction is active. In contrast, as pointed out above, temperatures deduced from infrared emission during convective-heating pyrolysis experiments should indicate actual surface temperatures. The present data (from infrared emission measurements) do not, however, differ greatly from earlier hot-plate temperatures. The implications of this fact are currently under investigation by the authors.

#### VI. The Relation Of Current Linear Pyrolysis Results To AP Propellant Combustion Phenomena

Linear pyrolysis data for AP may be viewed in two ways relative to propellant combustion.

First, the  $r$  vs  $T_s$  data observed may be considered as a strictly empirical correlation, one which might ultimately be of use as input data to propellant combustion models. Within this empirical view, the pyrolysis data stand, in and of themselves, as potentially useful characterizations of surface pyrolysis at high surface heating rates. Such an empirical characterization,

however, is useful only to the extent that it is incorporated virtually unaltered into deflagration models. These models might be expected to require coupling the pyrolysis characterization with additional aspects such as surface geometry, local temperature fields, etc. (8). Such use of empirical  $r$ - $T_s$  data has been infrequent and of doubtful success. Much more common have been quasi-Arrhenius treatments of the combined pyrolysis of propellant fuel and oxidizer ingredients.

From a second viewpoint, the  $r$  vs.  $T_s$  data derived from linear pyrolysis studies represent experimental manifestations of fundamental chemical kinetic processes coupled with mass and heat transport processes. Such a viewpoint leads to seeing the linear pyrolysis process as a phenomenological bridge between lower temperature, lower rate, bulk pyrolysis processes and the higher temperature, higher rate pyrolysis which apparently occurs during propellant deflagration. In this context, the aim of linear pyrolysis experiments is to diagnose the mechanism of the linear pyrolysis process and, thereby, to allow mechanistic extrapolation of linear pyrolysis data ( $r = 0.05$  cm/sec) to useful, combustion situations. ( $r = 0.1$  to  $1.0$  cm/sec).

Little extrapolation of linear pyrolysis *per se* is evident in the literature, probably because the scattered diverse results obtained to date have not encouraged linear pyrolysis experiments aimed at more than empirical correlation of  $r$ - $T_s$  data.

In this regard, further use of the pyrolysis approach reported here is attractive owing to the promisingly low data scatter observed. Environmental effects (e.g., pressure, composition) on linear pyrolysis might be investigated, for example, to complement and extend the very few prior investigations of these effects (1, 5).

Recently, two attempts to relate linear pyrolysis data to low-temperature isothermal pyrolysis data have been made. One of these (24) aims specifically at reconciling isothermal pyrolysis, linear pyrolysis, and low-pressure combustion data, using fundamental views of sublimation based on isothermal pyrolysis data. The other (25) employs linear pyrolysis data as a means for checking, at intermediate temperatures and reaction rates, a proposed extrapolation of isothermal pyrolysis data to propellant deflagration conditions. That is, in both approaches, linear pyrolysis data are invoked for corroborating

\* Calculated by scaling the emitter density from solid-phase to gas-phase and assuming a gas layer of uniform-temperature and composition at the AP monopropellant flame temperature (ca.  $970^\circ\text{C}$ ., Ref. 21,23).

\*\*The products of the AP monopropellant flame do not apparently emit strongly at 3.1 microns (9) nor does the hot gas jet used in this study.

models stimulated and formulated by direct reference to bulk, isothermal pyrolysis data. No significant new information, either mechanistic concepts or numerical data, is introduced into these approaches from observations on linear pyrolysis processes, though some mechanistic conjectures are suggested in order to reconcile linear pyrolysis data with the approaches taken.

Both of these attempts lead to apparent activation energies of about 30 Kcal/mole for AP linear pyrolysis. Allowances are made, however, for phenomena which might yield different activation energies for linear pyrolysis experiments. The present data, in supporting an apparent 20 Kcal/mole value for linear pyrolysis, suggest further modeling within and probably beyond the confines of the two approaches cited. Such work is a prerequisite for validating attempts to extrapolate low-temperature, low-rate data to propellant situations using approaches based on isothermal pyrolysis results (or even linear pyrolysis results).

#### References

1. Andersen, W.H. and Chaiken, R.F., "Detonability of Solid Composite Propellants," ARS Journal, Vol. 31, No. 10, October 1961, pp. 1379-1387.
2. Coates, R.L., "Linear Pyrolysis Rate Measurements of Propellant Constituents," AIAA Journal, Vol. 3, No. 7, July 1965, pp. 1257-1261.
3. Guinet, M., "Vitesse lineaire de pyrolyse du perchlorate d'ammonium en ecoulement unidimensionnel," La Recherche Aerospatiale, No. 109, Nov.-Dec. 1975, pp. 41-49.
4. Lieberherr, J-F. (O.N.E.R.A., France), Personal Communication, Sept. 1967.
5. Lieberherr, J-F, "High Temperature Pyrolysis of Ammonium Perchlorate," T.P. 612, 1968, O.N.E.R.A., Chatillon, France (Presented at Twelfth Symposium (International) on Combustion (The Combustion Institute), Poitiers, France, July 14-20, 1968).
6. von Elbe, G., King, M.K., McHale, E.T., Macek, A., Friedman, R., and Levy, J.B., "Chemical-Kinetic and Physical Processes in Composite Solid Propellant Combustion," NASA Contractor Rep't 66307, Jan. 1967, Atlantic Research Corp., Alexandria, Va.
7. McAlevy, R.F., III, and Hansel, J.G., "Linear Pyrolysis of Thermoplastics in Chemically Reactive Environments," AIAA Journal, Vol. 3, No. 2, Feb. 1965, pp. 244-249.
8. Powling, J., "Experiments Relating to the Combustion of Ammonium Perchlorate-Based Propellants," Eleventh Symposium (Int.) on Combustion, The Combustion Inst., Pittsburgh, 1967, pp. 447-456.
9. Powling, J., and Smith, W.A.W., "Measurement of the Burning Surface Temperatures of Propellant Compositions by Infra-red Emission," Comb. & Fl., Vol. 6, No. 3, Sept. 1962, pp. 173-181.
10. Nachbar, W., and Williams, F.A., "On the Analysis of Linear Pyrolysis Experiments," Ninth Symposium (Int.) on Combustion,
11. McAlevy, R.F., III, Lee, S.Y., and Smith, W.H., "Linear Pyrolysis of Polymethylmethacrylate during Combustion," AIAA Journal, Vol. 6, No. 6, June 1968, pp. 1137-1142.
12. Pearson, G.S., Comments on Ref. 8, Eleventh Symposium (Int.) on Combustion, The Combustion Inst., Pittsburgh, 1967, p. 456.
13. Barrere, M. and Williams, F.A., "Analytical and Experimental Studies of the Steady-State Combustion Mechanism of Solid Propellants" T.P. 240, 1965, O.N.E.R.A., France (Presented at the 25th Meeting of the AGARD Propulsion and Combustion Panel, La Jolla, California, April 1965).
14. Hansel, J.G. and McAlevy, R.F., III, "Energetics and Chemical Kinetics of Polystyrene Surface Degradation in Inert and Chemically Reactive Environments," AIAA Journal, Vol. 4, No. 5, May 1966, pp. 841-848.
15. Planck, M., The Theory of Heat Radiation, Dover, New York, 1959, p. 176.
16. Powling, J. and Smith, W.A.W., "The Surface Temperature of Ammonium Perchlorate Burning at Elevated Pressures," Tenth Symposium (Int.) on Combustion, The Combustion Inst., Pittsburgh, 1965, pp. 1373-1380.
17. Sparrow, E.M. and Cess, R.D., Radiation Heat Transfer, Brooks/Cole, Belmont, Cal., 1966, pp. 67-69.
18. Hall, A.R. and Pearson, G.S., "Ammonium Perchlorate: A Review of its Role in Composite Propellant Combustion," Tech. Report 67/1, Rocket Prop. Establ. (Westcott), England, Jan. 1967, pp. 55-59.
19. Frank-Kamenetskii, D.A., Diffusion and Heat Exchange in Chemical Kinetics, Princeton Univ. Press, Princeton, 1955.
20. Chaiken, R.F., Andersen, W.H., Barsh, M.K., Mischuck, E., Moe, G., and Schultz, R.D., "Kinetics of the Surface Degradation of Polymethylmethacrylate," J.Chem.Phys., Vol. 32, No. 1, Jan 1960, pp. 141-146.

21. Levy, J.B. and Friedman, R., "Further Studies of Pure Ammonium Perchlorate Deflagration," Eighth Symposium (Int.) on Combustion, Williams & Wilkins, Baltimore, 1962, pp. 663-677.
22. Steinz, J.A., Stang, P.L., and Summerfield, M., "The Burning Mechanism of Ammonium Perchlorate-Based Composite Solid Propellants," AIAA Preprint 68-658 (Presented at 4th Propulsion Joint Specialist Conference, Cleveland, June 1968).
23. Adams, G.K., Newman, B.H., and Robins, A.B., "The Combustion of Propellants Based Upon Ammonium Perchlorate," Eighth Symposium (Int.) on Combustion, Williams & Wilkins, Baltimore, 1962, p. 694.
24. Jacobs, P.W.M. and Powling, J., "The Role of Sublimation in the Combustion of Ammonium Perchlorate Propellants," Abstracts of Papers for Twelfth Symposium (Int.) on Combustion, The Combustion Inst., Pittsburgh, 1968, pp. 99-100 (Paper not presented at Symposium).
25. Waesche, R.H.W., "Research Investigation of the Decomposition of Composite Solid Propellants," G910476-24, United Aircraft Research Labs., East Hartford, Sept. 1968.

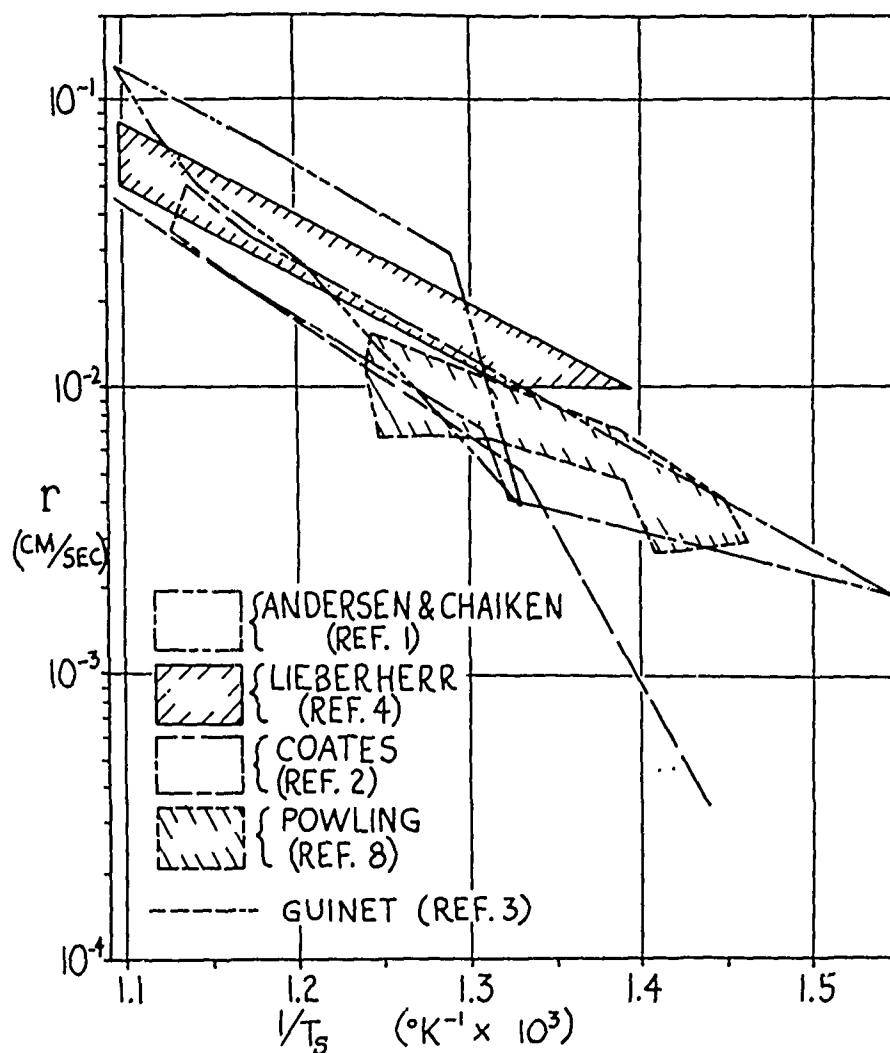


FIG.1 PRIOR AP LINEAR PYROLYSIS RESULTS

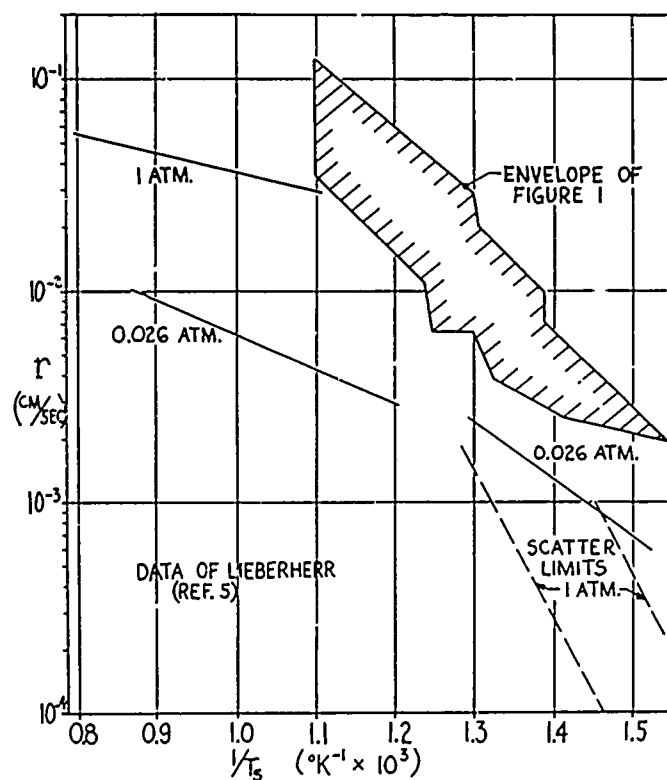


FIG.2 RECENT EXTENDED AP LINEAR PYROLYSIS RESULTS (SELECTED PRESSURES) OF LIEBERHERR WITH ENVELOPE OF PRIOR RESULTS

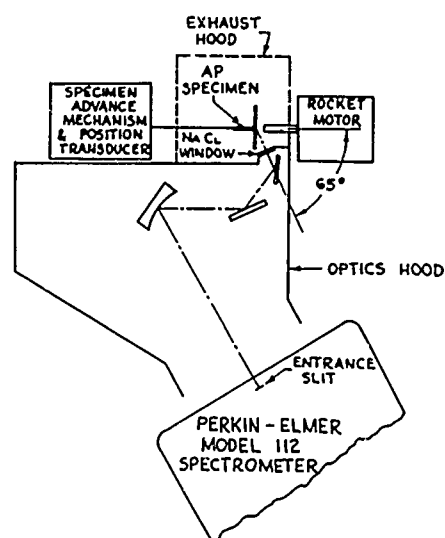


FIG.3 EXPERIMENTAL APPARATUS FOR AP LINEAR PYROLYSIS VIA CONVECTIVE HEATING WITH INFRARED RADIOMETRY

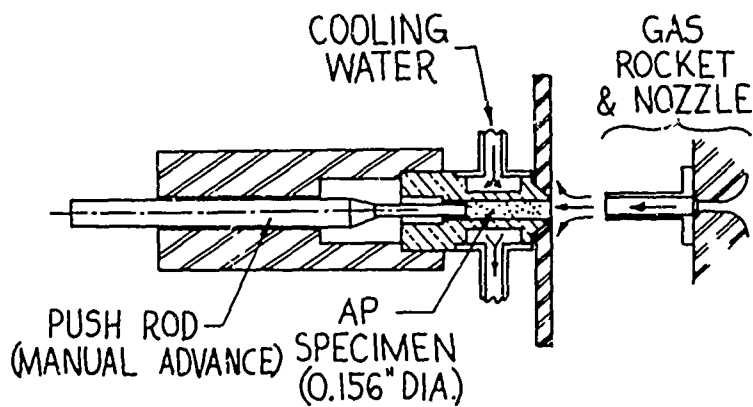


FIG.4 DETAIL OF SPECIMEN HOLDER  
FOR AP LINEAR PYROLYSIS APPARATUS

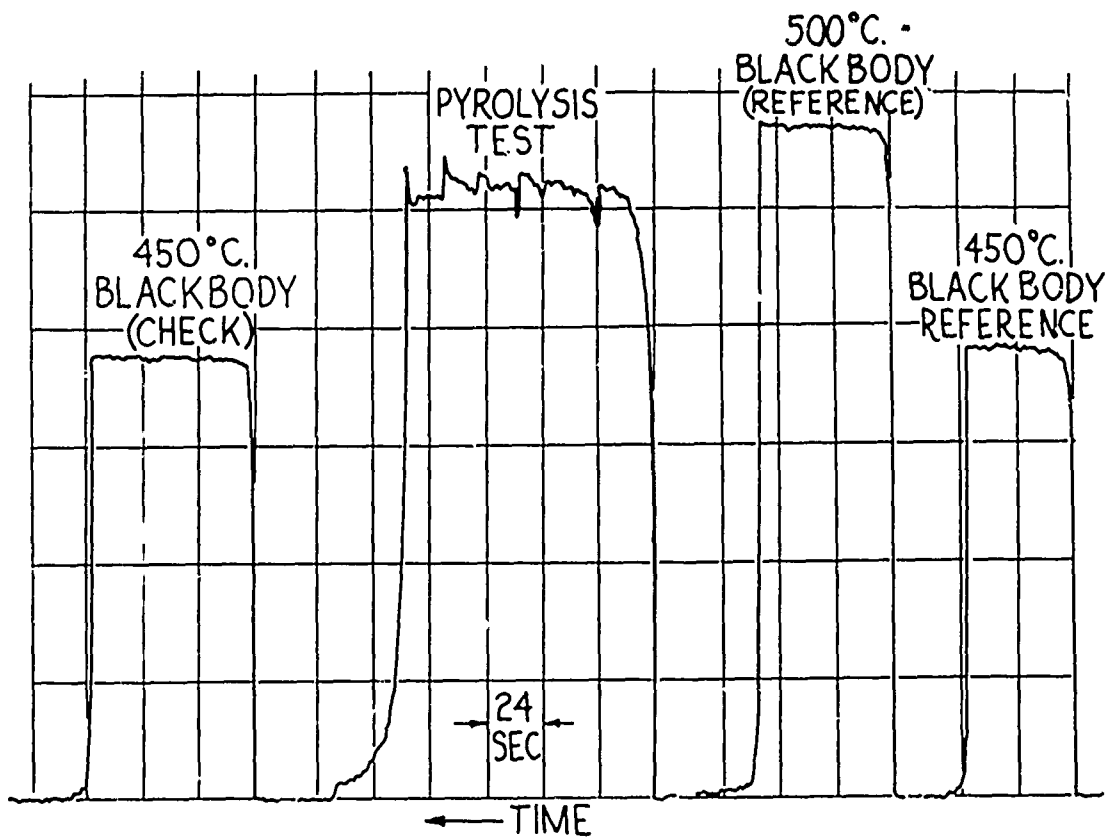


FIG.5 TYPICAL RECORD OF MONITORED  
INFRARED RADIATION (3.1 MICRONS)

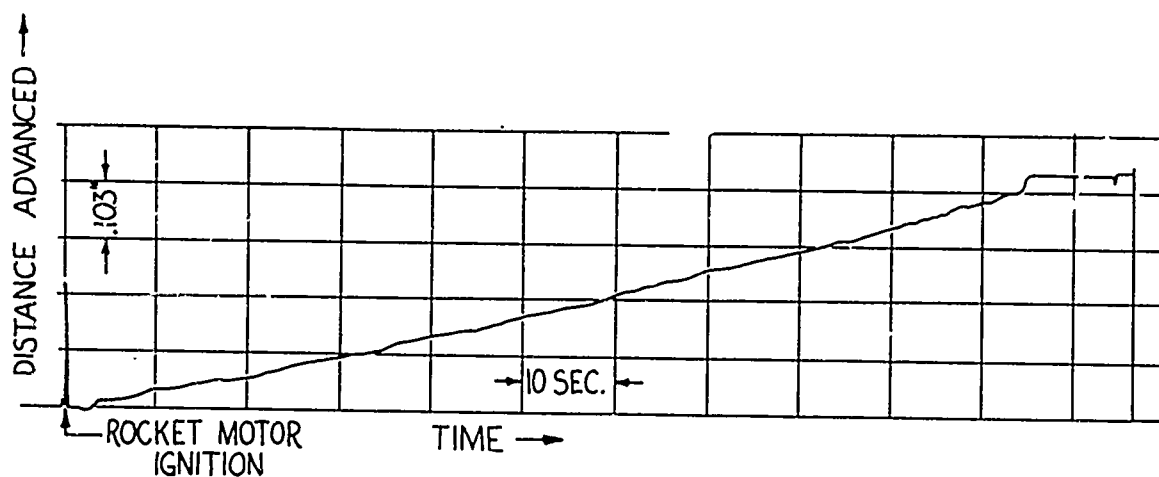


FIG. 6 TYPICAL RECORD OF SPECIMEN DISPLACEMENT HISTORY DURING LINEAR PYROLYSIS TEST

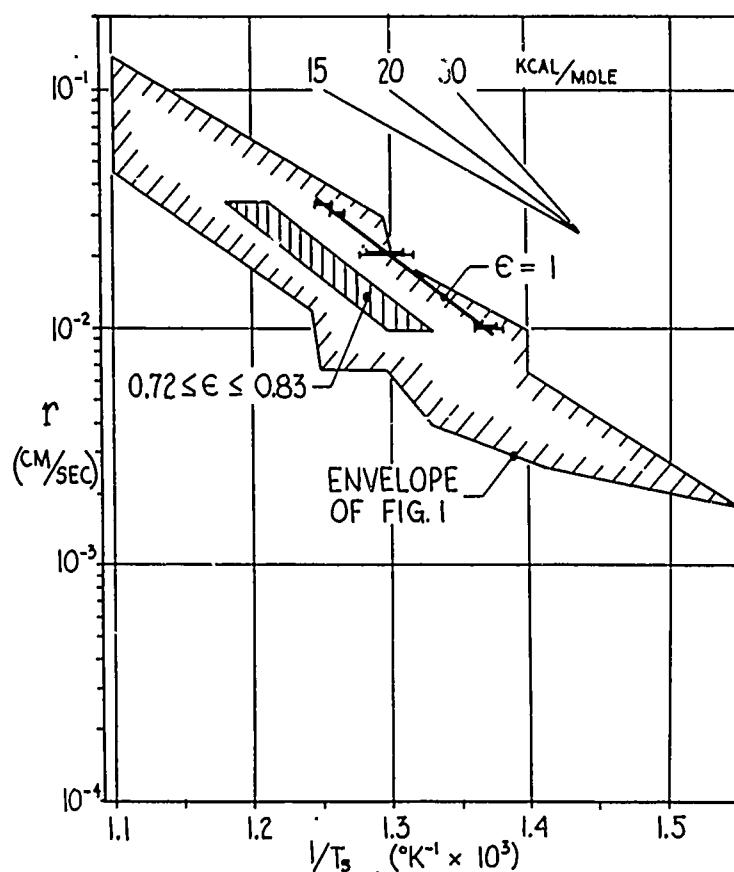


FIG. 7 PRESENT AP LINEAR PYROLYSIS RESULTS (WITH ENVELOPE OF OTHERS' RESULTS)

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13. ABSTRACT Ammonium perchlorate (AP) specimens were exposed to various levels of convective surface heating at one atmosphere ambient pressure. Surface regression rates were measured and, simultaneously, surface temperatures were determined by measuring the infrared emission near $3.1\mu$ . These data represent the first AP linear-pyrolysis characteristics obtained by means of convective surface heating. Previously, linear pyrolysis was obtained by pressing specimens against heated plates (solid and porous) and heated wire meshes. The subject data agree with some, and disagree with other, of these previous data. The usefulness of convective surface heating and radiometric techniques are evaluated. It is demonstrated that preliminary experiments are required to support their use in linear pyrolysis studies. According to the evaluation, previous radiometric work dealing with surface decomposition is open to substantial question. It is concluded that the subject techniques are viable and offer experimental compliments to other methods, but that none of the current techniques are without substantial shortcomings. Means of incorporation of AP linear pyrolysis results into theoretical models of the propellant deflagration process are discussed.		

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Ammonium Perchlorate Linear Pyrolysis Composite Propellants Solid Propellant Oxidizer						

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